Modeling of Water Soluble Organic Content in Produced Water

Oak Ridge National Laboratory, ChevronTexaco, Conoco-Phillips, Shell and Statoil

Objective

Specific Concerns with Off-Shore Production of Crude Oil

- *The volume of produced water is very large. The locations are remote, making remediation complex and expensive.*
- *NPDES permits restrict recoverable oil and grease to 42 mg/L daily maximum, 29 mg/L on average.*
- *The amounts and types of water soluble organics are not well known, particularly in the case of new wells.*
- *Crude oil from off-shore contains a large amount of polar material, which are more water soluble than non-polar organic compounds.*

Our goal is to design a computational tool for the prediction of water soluble organic compounds in produced water.

The ability to predict concentration based on simple field-based parameters such as pH, temperature, pressure, and geographical location will allow better planning for organic removal. Targeting specific compounds or classes of compounds in produced water will be more efficient and cost effective than current methods.

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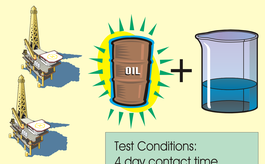
Empirical Analysis of Water Characterization Experiments

Gulf of Mexico Crude Oil



Simulated Gulf of Mexico Brine

Test Conditions:
4 day contact time
pH (4.5 to 9.5)
Pressure (1 to 60 bar)
Temperature (25 to 75°C)
Salinity (45 to 115 ppt)
Water Cut (20 to 80%)

Characterization of Produced Water

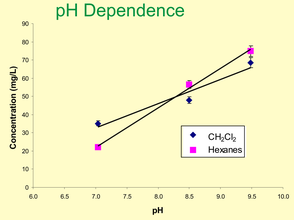
Differentiate semi-volatile, water-soluble organic (WSO) compounds by chemical classification and size, to derive lumped parameter properties for use in a thermodynamic model.

Aliphatic, Aromatic, Polar
C_6-C_{10}, C_{10}-C_{20}, C_{20}-C_{28}

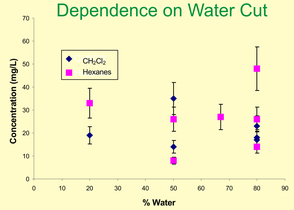
Measure the effects of physico-chemical conditions on solubility of WSO compounds.

pH
Temperature
Pressure
Salinity
Water to oil ratio
Origin of crude oil

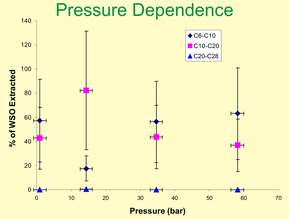
pH Dependence



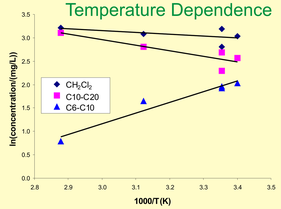
Dependence on Water Cut



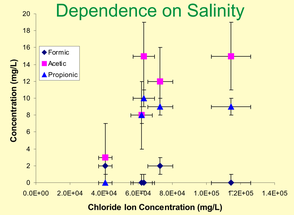
Pressure Dependence



Temperature Dependence



Dependence on Salinity



Effect of Oil Chemistry

Components	Crude#1	Contact Produced Water
Aliphatic	67 ± 8%	1 ± 1%
Aromatic	18 ± 11%	1 ± 1%
Polar	15 ± 3%	96 ± 3%
	Crude#2	Contact Produced Water
Aliphatic	26, 40,6%	5 ± 2%
Aromatic	57, 45,7%	50 ± 20%
Polar	17, 13.7%	40 ± 20%

Thermodynamic Liquid-Liquid Equilibrium Model

ORNL used a chemical equilibrium model to fit PERF characterization data because the empirical analysis cannot be used for predictions.

The model incorporates two liquid phases because experiments measured semi-volatile components only. The distribution between aqueous and hydrocarbon phases depends on the ratio of the activity coefficients of the organic compound in each phase.

The model includes:
- *Interactions between aqueous phase components described by non-random two liquid activity coefficients (NRTL).*
- *pH dependence was the most important factor in WSO solubility (arising from acid-base equilibria).*
- *Salinity (Debye-Huckel description of ionic activity coefficients).*

Advantage of thermodynamic model is that it can be extended to include
- *Temperature dependence (through model for activity coefficients).*
- *Pressure dependence/Volatile components (incorporation of gas phase).*
- *Mathematically simple.*

Difficulty in modeling using thermodynamic equilibrium comes in the definition of the chemical system.
- *Oil/brine mixtures have over 1000 components.*
- *Distribution of components will vary with well location and time.*
- *Difficult to generalize NRTL coefficients to multicomponent mixtures.*

UNIFAC description of organic compounds
- *Based on functional group analysis (e.g., CH, OH, C=C, etc.)*
- *Will test variation of activity coefficients with size, chemical characteristics*
- *Includes temperature dependence*
- *Parameters for functional groups of interest in oil/brine chemistry are already available.*
- *Can use mathematical platform already developed.*

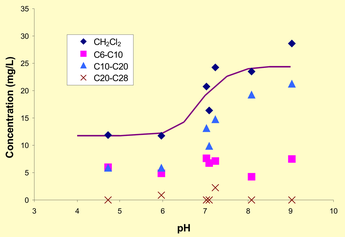
System $F z_i \quad L x_i \quad W u_i \quad W d_i \qquad \beta = \frac{W}{F}$

Equilibria $u_i \quad Kw_i x_i \qquad d_i = \frac{u_i Ka_i \Gamma_i}{H} \qquad \alpha_i := \frac{Ka_i}{H + Ka_i} \qquad \Gamma_i = \frac{\gamma H \gamma A_i}{\gamma HA}$

Rachford-Rice Equation $\sum_{i=1}^{c} \frac{z_i (-H + Kw_i H + Kw_i Ka_i \Gamma_i)}{-\beta H + \beta Kw_i H + \beta Kw_i Ka_i \Gamma_i + H} = 0$

Constraints $\sum_{i}^{c} x_i \; 1, \quad \sum_{i}^{c} z_i \; 1, \quad \sum_{i}^{c} (u_i \; d_i) \; 1$

NRTL Activity Coefficients



Using Statistics for Predictions

A deterministic model of solubility depends on a good knowledge of oil characteristics and brine characteristics over time. If input data is missing or is of poor quality, there is no reliable way to quantify the error in the prediction..

A statistical model uses the uncertainty in input variables to calculate confidence limits on predictions.

Steps in modeling include:
- *Compile data from other oil fields*
- *Include field-based variables in the analysis (e.g., Geochemistry)*
- *Assess importance of variables to solubility. Calculate correlations between variables.*
- *Predict output distribution of solubilities based on a randomly generated distribution of input variables.*

Uncertainties in the predictions will be reduced by better knowledge of input variables, e.g, pH, temperature....

T.I. Utvik, Chemosphere 29, 2593-2606 (1999)